Convergence of Green Iterations for Schrödinger Equations

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The second author dedicates this article to the fond memory of his teacher and friend Clasine van Winter 1929-2000.

Abstract

For a time-independent Schrödinger equation with Hamiltonian operator $H = -\Delta + V$ on $L^2(\mathbb{R}^{3N})$ we call $\mathcal{G}_z = R_z V$, the Green function operator, where R_z is the resolvent of $-\Delta$. We consider an iteration scheme that is based on the operator $\mathcal{G}_z$. Under standard conditions on the potential V, which include the Coulomb interaction, we prove the convergence of the iteration to the ground state energy and eigenfunction when $N = 1$ or 2.

Key words: Coulomb potential, Kato Potential, Green Iteration, multi-particle Schrödinger.

1 Green Function Iterations

In this note we will consider the convergence of an iterative scheme for the time-independent, bound-state Schrödinger equation in $\mathbb{R}^3$:

$$H\phi = \lambda\phi, \tag{1}$$

where H is the Hamiltonian operator corresponding to N particles with interactions:

$$\begin{aligned} H &= -\Delta + V \\ &= -\sum_{i=1}^{N} \Delta_i - \sum_{\alpha<\beta}^{N} V_{\alpha\beta}(x_{\alpha\beta}), \end{aligned} \tag{2}$$

where $x_{\alpha\beta} \in \mathbb{R}^3$ are the relative positions of the particle pairs. Here Δ_i acts on $x_i \in \mathbb{R}^3$ and H is considered as acting on the Hilbert Space $\mathcal{H} = L^2(\mathbb{R}^{3N})$. Here and throughout $||\cdot||$ will denote the L^2 norm. (We could also consider a center of mass reduction $\mathcal{H} = L^2(\mathbb{R}^{3N-3})$, but this would not effect the analysis.) The interaction potential V is considered as a multiplication operator on this space and all eigenfunctions will be assumed to be normalized in this space.

Denote by R_z the resolvent of $-\Delta$, i.e.

$$R_z = (-\Delta - z)^{-1} .$$

Then the Green function operator is defined by:

$$\mathcal{G}_z = -R_z V . \tag{3}$$

The iteration is defined by:

$$\psi_{i+1} = \frac{\mathcal{G}_{z_i}\psi_i}{||\mathcal{G}_{z_i}\psi_i||} \tag{4}$$

$$z_{i+1} = \langle H\psi_{i+1}, \psi_{i+1}\rangle, \tag{5}$$

where we will make the restriction $z_i < 0$. Note that any discrete eigenvalue-eigenfunction pair, (λ, ϕ), for the operator H is a fixed point for the iteration (4) & (5). We will focus primarily on the ground state eigenvalue $\lambda^* = \min(\sigma(H))$ and the corresponding eigenfunction ϕ^*. For the potential functions we will consider, it is known that this pair exists and is unique.

The chief motivation for using this iteration is that R_z for $\mathfrak{Re}z < 0$ has an integral representation and thus is well-suited for computations. An integral representation approximation is usually substituted for the Rayleigh quotient (5) as well (see e.g. [5]).

The exact origin of this iteration scheme is unclear, but the operator $\mathcal{G}_z$ appeared as early as [10]. Since [16], [6], and [7] it has been a standard tool for characterizing the discrete spectrum (bound states) of H. As the basis for a numerical method in quantum mechanics, the first use of this iteration is attributed to [8, 9]. Single-particle variants have been used in e.g. [5]. Using this iteration within the framework of [2, 3] for computing in high dimensions without the curse of dimensionality may allow direct computations of ϕ in (1).

We will assume throughout that each interaction potential V satisfies the following two assumptions:
(A) *Each $V_{\alpha\beta}$ satisfies:*

$$V_{\alpha\beta} \in L^2(\mathbb{R}^3) + L^\infty(\mathbb{R}^3),$$

i.e. $V_{\alpha\beta}(x) = V_1(x) + V_2(x)$ where $V_1 \in L^2$ and $V_2 \in L^\infty$.
and

(B) *The L^∞ part of each $V_{\alpha\beta}$ can be taken to be arbitrarily small in the L^∞ sense.*

Note assumptions **(A)** and **(B)** include the case of M electrons and K nuclei interacting with Coulomb potentials:

$$\begin{aligned} H &= -\Delta + V^{ne} + W^{ee} \\ &= -\sum_{i=1}^{M} \Delta_i - \sum_{i+1}^{M} \sum_{\nu=1}^{K} \frac{Z_\nu}{|x_i - a_\nu|} + \sum_{i<j}^{M} \frac{1}{|x_i - x_j|}. \end{aligned} \tag{6}$$

Here a_ν are the (fixed) positions of the nuclei.

We have then our main result:

Theorem 1.1 *Suppose that V satisfies assumptions* **(A)** *and* **(B)**, *and that $N = 1$ or 2. Then there exists $\delta > 0$ such that if $|z_0 - \lambda^*| < \delta$ and any $||\psi_0 - \phi^*|| < \delta$, then the iteration $\{\psi_i, z_i\}_{i=0}^{\infty}$ defined by (4) & (5) converges to (ϕ^*, λ^*).*

When $N > 2$, the operator $\mathcal{G}_z$ is no longer compact, so our argument breaks down. We discuss the issues for $N > 2$ further in Section 4.

2 Background Material

Definition 2.1 *We will say that an operator A is* bounded *by B if $\mathcal{D}(B) \subset \mathcal{D}(A)$ and the inequality:*

$$||A\psi|| \leq a||B\psi|| + b||\psi|| \tag{7}$$

holds for some $a, b > 0$ and all $\psi \in \mathcal{D}(B)$. Furthermore, we say that A is ϵ-bounded by B if for any $a > 0$ there exists b such that (7) holds.

The term infinitesimally bounded, or, bounded with absolute bound 0 are also commonly used for ϵ-boundedness. In classical work, Kato [10] and Rellich [14] showed

Theorem 2.2 (Kato-Rellich) *For potentials, V, that are ϵ-bounded by Δ, the operator $H = -\Delta + V$ has a unique self-adjoint extension and is bounded below, that is, $\lambda^* = \min \sigma(H) > -\infty$.*

Further, Kato showed that for a potential $V = \sum V_\alpha$ in $\mathbb{R}^{3N}$ assumption **(A)** implies inequality (7), thus putting the Hilbert space formulation of non-relativistic quantum mechanics on a sound mathematical footing. Since then it has been shown that H has a unique self-adjoint extension if only (7) holds for some $a < 1$ (see [12, Theorem X.12]).

From the next result it is clear that the inequality (7) is important in the present context.

Proposition 2.3 *Inequality (7) implies that $\mathcal{G}_z$ is a bounded operator on L^2 for $\mathfrak{Re} z < 0$.*

To see this consider $\psi = R_z\phi$ where $\phi \in L^2$. Then we have:

$$\begin{aligned} ||VR_z\phi|| &\leq a||\Delta R_z\phi|| + b||R_z\phi|| \\ &\leq (a||\Delta R_z|| + b||R_z||)||\phi|| \\ &\leq (a + b|\mathfrak{Re}z|^{-1})||\phi||. \end{aligned} \tag{8}$$

The claim then follows since VR_z is the adjoint of $\mathcal{G}_z = R_zV$. □

Further, the following result will play a crucial role. Let $\sigma_c(H)$ denote the continuous spectrum of H.

Theorem 2.4 *Suppose V satisfies assumptions* **(A)** *and* **(B)** *and $N = 1$ or 2. Then for any $z \in \mathbb{C} \setminus \sigma_c(H)$, $\mathcal{G}_z$ is a compact operator on $L^2(\mathbb{R}^{3N})$.*

This theorem is a classical result [6, 16, 7, 4]. A proof in the case $N = 1$ can now be found in textbooks [15, Lemma 8.7.4]. When $N > 2$, however, the operator $\mathcal{G}_z$ is no longer compact [7, 13].

Next we consider the perturbation theory of Schrödinger operators where inequality (7) also plays a key role.

Definition 2.5 *([13, p. 14],[11, p. 375]) Let R be a connected domain in the complex plane and suppose $T(\beta)$ is a closed operator with nonempty resolvent set for each $\beta \in R$. We say that $T(\beta)$ is an* analytic family of type (A) *if and only if*

(i) The operator domain of $T(\beta)$ is some set D independent of β.

(ii) For each $\psi \in D$, $T(\beta)\psi$ is analytic function of β (with values in L^2).

We find the following lemma in Reed and Simon [13, p. 17]:

Lemma 2.6 *Let H_0 be a closed operator with nonempty resolvent set and V a potential function. Define $H_\beta = H_0 + \beta V$. Then H_β is an analytic family of type (A) near $\beta = 0$ if and only if V is H_0 bounded. Further, if V is ϵ-bounded by H_0, then H_β is an entire family.*

We will also use the following (See [13, Theorem XII.13].):

Theorem 2.7 *Suppose $T(\beta)$ is an analytic family of type (A) and E_0 is a discrete eigenvalue of $T(0)$ with multiplicity m. Then for all β in a neighborhood of 0, $T(\beta)$ has exactly m eigenvalues, counting multiplicities, in a neighborhood of E_0 and these eigenvalues depend analytically on β.*

Finally, note that R_z is an analytic family in z, so $\mathcal{G}_z = R_zV$ is an analytic family and thus its discrete eigenvalues depend analytically on z.

3 Proof of Main Result

Since $\mathcal{G}_{\lambda^*}$ is compact (for $N = 1$ or 2), its spectrum consists of eigenvalues. Furthermore, the only possible accumulation point for these eigenvalues is 0. Note that ϕ^* is an eigenfunction of $\mathcal{G}_{\lambda^*}$ with eigenvalue 1. Thus we know that $||\mathcal{G}_{\lambda^*}|| \geq 1$.

Proposition 3.1 $||\mathcal{G}_{\lambda^*}|| = 1$

PROOF: Because the spectrum consists of eigenvalues, we know that $||\mathcal{G}_{\lambda^*}|| > 1$ if and only if $\mathcal{G}_{\lambda^*}$ has an eigenvalue greater than 1 in absolute value, i.e.:

$$\mathcal{G}_{\lambda^*}\,\xi = e\,\xi$$

where $|e| > 1$. Rearranging this equation we see that it is equivalent to:

$$(-\Delta + \frac{1}{e}V)\xi = \lambda^*\,\xi.$$

In other words, ξ is an eigenfunction of the modified Hamiltonian $H_e = -\Delta + \frac{1}{e}V$ with eigenvalue $\lambda^* < 0$. Self-adjointness of H_e and positivity of $-\Delta$ implies that $e > 1$. Since H_e is an entire family in e, we can calculate directly:

$$\begin{aligned}\frac{\partial}{\partial e}\langle H_e\xi, \xi\rangle &= \frac{\partial}{\partial e}\langle\frac{1}{e}V\xi, \xi\rangle \\ &= -\frac{1}{e^2}\langle V\xi, \xi\rangle,\end{aligned}$$

for any $\xi \in L^2$. Since $-\Delta$ is a positive operator, it is follows that $\langle V\xi, \xi\rangle$ must be negative for any bound state of H_e. Thus $\langle H_e\xi, \xi\rangle$ is an increasing function of e. Next consider that $\langle H\xi, \xi\rangle \geq \lambda^*$ for any ξ. Together these facts imply that the ground state energy of H_e is greater than λ^*. Thus λ^* cannot be in the spectrum of H_e. This is a contradiction which proves Proposition 3.1. □

PROOF OF THE THEOREM: Returning to Theorem 1.1, we have that the spectrum of $\mathcal{G}_{\lambda^*}$ consists of eigenvalues. By the Proposition above these eigenvalues are contained in the interval $[0, 1]$ and ϕ^* is an eigenfunction with eigenvalue 1. Suppose that $\mathcal{G}_{\lambda^*}$ has another eigenfunction ξ with eigenvalue 1. It follows easily that ξ is an eigenfunction of the original Hamiltonian H with eigenvalue λ^*.

Since the ground state is known to be unique, $\xi = \phi^*$. Since the eigenvalues of $\mathcal{G}_{\lambda^*}$ are discrete there is a second largest eigenvalue $d < 1$. Thus we can employ the standard power method argument; all functions in $L^2(\mathbb{R}^3) - \text{span}(\phi^*)$ are contracted by $\mathcal{G}_{\lambda^*}$ by a factor at least as small as $d < 1$ and so they converge to 0 by the iteration, leaving only ϕ^*. Thus we have convergence for $\mathcal{G}_{\lambda^*}$.

Finally, consider the fact that $\mathcal{G}_z$ is an analytic family of type (A) for z in the resolvent set of Δ, so its spectrum depends continuously on z. Thus, we may choose $\delta > 0$ so that for any $|z - \lambda| \leq \delta$, $\mathcal{G}_z$ has maximal eigenvalue $e_1 \approx 1$ and $e_2 \approx d$ and $e_2 + \epsilon < e_1$ for some $\epsilon > 0$. Thus $\mathcal{G}_z$ contracts all functions except the span of the eigenfunction corresponding to the largest eigenvalue $e_1 \approx 1$.

Further, the eigenfunctions of an analytic family of type (A) also depend analytically on the operator [13, p. 23]. Thus we may further restrict δ so that $|\phi_z^* - \phi^*| < \epsilon$ where ϕ_z^* is the eigenfunction of $\mathcal{G}_z$ corresponding to $e_1 \approx 1$. It is known that if $|\phi_z^* - \phi^*| < \epsilon$ then $|\langle H\psi_{i+1}, \psi_{i+1}\rangle - \lambda^*| < C\epsilon^2$. Thus by choosing δ sufficiently small we can guarantee the $|z_{i+1} - \lambda^*| < |z_i - \lambda^*|$. This in term implies that $||\psi_{i+1} - \phi^*|| < ||\psi_i - \phi^*||$.

□

It is clear that if we modify the iteration so that z_i remains in a neighborhood of λ^*, then the iteration converges for any $\psi_0 \in L^2$ satisfying $\langle \psi_0, \phi\rangle \neq 0$.

4 Concluding Remarks

We have neglected

1. a factor of 1/2 in front of Δ in the definition of the Hamiltonian H in (2),
2. the spin variables, and
3. the antisymmetry constraint.

Although these are necessary to compute physically meaningful eigenfunctions and eigenvalues, they do not effect the proof.

One might hope to use the iteration to find other eigenvalues and eigenvectors, as is done with usual power method iterations combined with Gram-Schmidt orthogonalization. However, in this case the eigenvectors of $\mathcal{G}_\lambda$ except for the fixed point ϕ are not eigenfunctions of the original problem, they instead are eigenfunctions of H_e for some e. Thus we cannot simultaneously locate the first n energy levels using this iteration. Rather we would have to first locate the ground state, then the second lowest energy, etc.. In this scheme, it could be hoped that some advantage could be gained by using the first iteration to locate an approximation to the second highest state, and the second iteration to approximate the third highest state, and so on.

Of course one would like to apply this iteration for $N > 2$. The rapid decay of bound states (due primarily to Agmon[1]) justifies restriction of the eigenfunctions to a bounded domain Ω, provided that the domain is reasonably large. Numerical methods based on the iteration method (4) & (5) are thus formulated on a bounded domain, often a large cube, with Dirichlet boundary conditions. If the operator $\mathcal{G}_z$ with these restrictions is now compact even when $N > 2$, then the rest of our convergence proof goes through. We believe this to be the case, but have not proven it.

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